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The Role of Melt Dynamics in Shear-enhanced Crystallization of Isotactic Polypropylene

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Beamline(s): X27C

Introduction: The strong deformations applied in traditional polymer processing applications are known to profoundly affect the crystallization rates, morphology, and material properties of semicrystalline polymers. Janeschitz-Kriegl and co-workers [1] devised a short term shearing protocol to separate the effect of primary nucleation from the growth of crystals at later times as well as minimize the reorientation of crystallites in the flow. They proposed a model in which "threadlike" precursors grow from point nucleation sites during shear. These threadlike precursors are postulated to grow with cylindrical symmetry. Oriented in the flow direction, they template further oriented crystalline growth. We performed experiments to characterize the lifetime the oriented precursors which template oriented crystallization.

Methods and Materials: Using a custom built apparatus, we are able to impose intense shear stresses on a polymer melt while maintaining a well defined thermal history [2]. A pneumatic actuator drives a piston into a reservoir of polymer melt forcing it to flow through a rectangular channel in our flow cell. After filling the channel with polymer melt, the flow cell is held at a temperature above the equilibrium melting point of the polymer to insure all crystallites are melted and to allow the polymer molecules in the melt to relax into an isotropic chain configuration. The polymer melt is then cooled to a crystallization temperature, Tc. A short shear pulse (short compared to the time for crystallization to begin at Tc) is applied to the sub-cooled melt. The ensuing crystallization is tracked using wide angle x-ray diffraction (WAXD). WAXD experiments were carried out at the Advanced Polymers Beamline (X27C) at NSLS using a Mar CCD camera that allows us to collect time resolved images of the powder diffraction patterns generated during this dynamic experiment. WAXD allows us to make quantitative comparisons of the crystalline orientation, degree of crystallinity, degree of crystallographic branching (cross-hatching), and identify the particular crystalline polymorphs of the iPP crystallites.

Modifying our normal short-term shearing protocol, we applied a short shear pulse to a melt held very near the nominal melting temperature (approx. 165 °C) where no crystallization occurs on a reasonable timescale. We then annealed the sheared melt at this temperature for some time t_a before cooling to a lower crystallization temperature Tc = 153 °C. By examining the degree of orientation of subsequent crystallization for various annealing times t_a, we can infer the relaxation time for the oriented precursors.

Initial rheo-optical experiments were carried out at our lab. WAXD experiments were used to corroborate our finding in optical studies.

Results: We first performed rheo-optical experiments in which we applied a wall shear stress of 0.12 MPa for 0.8 s. at T = 165 ºC and held at that temperature for 10, 30, 60, and 90 min. respectively before cooling to Tc = 153 ºC. We found that the birefringence grew during shear then completely relaxed on the order of 20 s. When cooling to the crystallization temperature, however, the birefringence begins to rise again, indicating the growth of oriented crystalline structures. The amount of birefringence induced decreases with increasing holding time, indicating the formation of less anisotropic crystallites.

To corroborate these hypotheses, we performed WAXD experiments corresponding to shearing at T = 165ºC and holding for 10, 30, and 60 min. before cooling to Tc = 153ºC. Powder diffraction patterns were acquired and qualitatively support our hypotheses. As we shear the material at T = 165ºC and hold for increasing lengths of time before cooling, it becomes obvious that the crystallization becomes less strongly oriented, just as we surmised from the rheo-optical data. Diffraction peaks become broader and weaker, showing a trend toward an isotropic crystalline phase. This observation is consistent with the concept that threadlike precursors formed during shear relax over time such that the threads become shorter and less aligned with the flow direction. Upon cooling, the subsequent crystal growth reflects the less oriented template, generating more spherulitic crystalline domains.

Conclusions: The results suggest that the relaxation of threadlike precursors is dictated by the melt rheology.

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